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Description

This invention relates to stabilised metallic oxides and particularly to those stabilised by coating with a hydrous yttrium oxide.

5 Zirconium oxide is used in the manufacture of ceramic materials and during such manufacture the oxide is heated during which the crystal form of the oxide changes from the normal room temperature monoclinic habit to tetragonal and cubic forms depending on the temperature to which the oxide is heated. Under normal conditions only the monoclinic form of pure zirconia is stable at room temperature and unless steps are taken to stabilise the tetragonal or cubic forms these revert to the monoclinic form on cooling.

10 The presence of at least some of these high temperature tetragonal and cubic crystal habits is desirable in ceramics and steps have been taken in the past to improve the stability of these crystalline forms at room temperature. Such steps have included mixing the zirconia with a stabilising agent which becomes incorporated in the zirconia on heating the doped oxide and exerts a stabilising influence on the crystal formed when it is cooled to room temperature.

15 One stabilising agent which has been used is yttrium oxide and a number of methods have been described for forming an intimate mixture of zirconia and yttria suitable for use in the manufacture of a ceramic material.

20 A problem which has been noted with ceramics prepared from zirconia stabilised with yttrium oxide is that the high strength produced initially is reduced by exposure to water at high temperature. This reduction in strength which herein is referred to as aqueous degradation limits the usefulness of yttria-stabilised zirconia ceramics in applications involving exposure to water at high temperature.

EP-A-0 403 104 produces zirconia ceramics with high resistance to attack by water at a temperature of at least 100 °C and comprises zirconia particles coated with a hydrous oxide of Yttrium and a hydrous oxide of Zr, Ti or Al.

25 It is an object of the present invention to provide a form of zirconia suitable for use in the manufacture of ceramics which have an increased resistance to aqueous degradation.

According to the present invention a composition suitable for use in the manufacture of a ceramic material comprises particulate zirconia in which the particles are coated with a hydrous oxide of yttrium and a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.

30 The compositions of the invention are easily sintered to form strong ceramic materials having good resistance to aqueous degradation.

According to the invention also a method of preparing a composition suitable for use in the manufacture of a ceramic material comprises coating particles of zirconia with a hydrous oxide of yttrium and with a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.

35 One preferred process comprises forming an acidic aqueous dispersion of zirconia particles, adding to the dispersion a water-soluble hydrolysable compound of yttrium and a water-soluble hydrolysable compound of manganese, iron, cobalt, nickel, copper or zinc and increasing the pH of the dispersion to form on the zirconia particles a coating comprising a mixture of hydrous oxides of yttrium and at least one of the aforementioned metals.

40 The yttrium oxide may be present as one layer with the oxide of the other metal forming a distinct layer or there may be present only one layer comprising a mixture of yttrium oxide with metal oxide.

45 Other inorganic oxides may also be present as a coating on the surface of the zirconia particles and in a preferred embodiment the zirconia particles are coated with an inner coating of hydrous titania, zirconia, hafnia or alumina or a mixture of these surrounded by an outer coating or coatings of yttrium oxide and an oxide of manganese, iron, cobalt, nickel, copper or zinc.

Particularly useful products comprise particulate zirconia having a size such that the majority of the particles have a diameter of less than or equal to 0.5 µm (microns) and preferably less than or equal to 0.2 µm (microns).

50 The amount of the hydrous oxide of yttrium employed depends upon the degree of stabilisation that it is desired should be imparted to the fired ceramic. Generally speaking the amount of the hydrous yttrium oxide present as coating will be less for a partially stabilised product than for a fully stabilised product. For a fully stabilised zirconia it has been found useful to provide in the coating from about 10 to about 20% by weight hydrous oxide of yttrium expressed as Y_2O_3 based on weight of zirconia. Generally, however, for optimum toughness a partially stabilised zirconia is preferred and a suitable composition has a coating of from about 2 to about 10% by weight hydrous oxide of yttrium expressed as Y_2O_3 based on weight of zirconia. Preferably the coating has from about 3 to 8% by weight hydrous oxide of yttrium and most preferably the amount of hydrous yttrium oxide is from about 3 to about 6% by weight.

The amount of hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc present is preferably from about 0.01 to about 4 molar %, more preferably from about 0.01 to about 2.0 molar % and most preferably from about 0.05 to about 1 molar % expressed as Mn, Fe, Co, Ni, Cu or Zn based on zirconia.

In accordance with the invention the particulate zirconia used to form the basis of the material to be used as a ceramic is preferably formed by the vapour phase oxidation/hydrolysis of a vaporised zirconium compound. Typical zirconium compounds which can be oxidised or hydrolysed in the vapour state are the zirconium halides, particularly zirconium tetrachloride and zirconium alkoxides. This is usually carried out by mixing the zirconium compound with an excess of heated oxygen or water vapour under such conditions that oxidation or hydrolysis of the zirconium tetrachloride takes place and the desired sized zirconia is obtained directly on cooling and separating from the gas stream. A preferred method of heating oxygen to react with the zirconium tetrachloride is to pass the oxygen through an electric arc between two electrodes supplied with electrical power at an appropriate voltage and amperage which commonly generates a so-called electrical plasma. This form of manufacture of the particulate zirconia has an advantage in that the product is obtained in the oxide form directly and that the oxidation process can be controlled so that the particle size of the product is as near to the crystal size as it is possible to obtain without extensive grinding of the product being required before treatment with the coating agents.

The product of the invention is obtained by treating the particulate zirconia in such a manner that the hydrous oxides are deposited as coatings on the surface of the particles of zirconia. Preferably the coating operation is carried out as a wet treatment process in which, initially, the zirconia particles are dispersed in water. It has been found that this dispersion can be effected directly by mixing the particles of zirconia with water without there being any requirement for a dispersing agent. This is advisable because it avoids any unnecessary contamination of the product with constituents of the dispersing agent. Generally speaking zirconia obtained from the vapour phase oxidation of the zirconium halide is highly acidic when mixed with water and depending on the exact form of the particles of zirconia can produce a dispersion pH of the order of 1 clearly indicating the highly acidic dispersions. It is sometimes preferable to commence the coating process with a zirconia dispersion having a higher pH. In such a process the pH of the zirconia dispersion is adjusted to the desired pH before the water soluble compounds which are precursors for the hydrous oxides are added.

As described the dispersion of the zirconia particles in water is effected normally by stirring with water in an amount such that the obtained dispersion contains zirconia in a concentration of up to 400 gpl. Usually the amount of zirconia is not less than 50 gpl zirconia and a convenient concentration to employ in practice is 200 gpl of zirconia. It is possible to improve the degree of dispersion by milling in, for example, a sand mill if desired.

To the aqueous dispersion of the particulate zirconia there is added a water soluble hydrolysable compound of yttrium in an amount sufficient to introduce on hydrolysis the required amount of hydrous oxide as a coating. Examples of water soluble hydrolysable compounds of yttrium which can be used include yttrium sulphate, yttrium chloride and yttrium nitrate. When it is desired to form a mixed coating of hydrous yttrium oxide together with a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc then a water soluble hydrolysable compound of at least one of these metals is also added to the zirconia slurry. Water soluble hydrolysable compounds which can be used include chlorides, sulphates and nitrates of these metals.

Any suitable means of mixing the aqueous dispersion of zirconia with the hydrolysable metal compounds can be used and a range of temperatures may be employed although it is preferred that the coating process be carried out at a temperature of from 10 °C to 70 °C.

After mixing of the hydrolysable metal compounds with the aqueous dispersion of zirconia, the pH of the dispersion is adjusted to precipitate the coating of hydrous oxides of yttrium and manganese, iron, cobalt, nickel, copper or zinc. The pH to which the dispersion is adjusted is from 3 to 12 and preferably from 7 to 10.

The neutralisation and increase in pH of the acidic aqueous dispersion either before or during the precipitation of the hydrous oxides preferably is carried out by the addition of an appropriate alkali to the aqueous dispersion. It is most convenient if the alkali is ammonium hydroxide since this does not introduce any objectionable metallic ions into the solution and waste ammonia can be driven off by heating. Stronger alkali such as an alkaline metal hydroxide can be used such as sodium hydroxide or potassium hydroxide. However when such alkaline metal hydroxides are used it is necessary to wash the product adequately to remove any contaminating alkali metal ions. Normally the product obtained should not contain an alkali metal impurity level greater than 0.01% by weight expressed as M₂O.

After deposition of the hydrous oxide coating the product is separated usually by filtering, washing as necessary and drying. If required the dried product may be ground or milled to remove any aggregation

that has occurred during processing.

In an alternative process the pH of a mixture of a water soluble hydrolysable compound of yttrium with an aqueous slurry of zirconia is adjusted to deposit a coating of hydrous yttrium oxide on the zirconia particles and these coated particles are subsequently coated with a layer of hydrous oxide of manganese, 5 iron, cobalt, nickel, copper or zinc by precipitation of the hydrous oxide from an aqueous solution of a hydrolysable compound of the respective metal substantially as described hereinbefore.

In a particularly preferred embodiment there is also provided on the zirconia particles an inner coating of a hydrous oxide of titanium, zirconium, hafnium or aluminium. This coating can be provided in substantially similar manner to that employed for producing coatings of the other hydrous metal oxides by 10 hydrolysis of water soluble compounds such as titanyl sulphate, titanyl aluminium sulphate, titanium oxychloride, zirconium chloride, zirconium sulphate, hafnium chloride, aluminium sulphate, aluminium nitrate or sodium aluminate. The coating with a hydrous oxide of titanium, zirconium, hafnium or aluminium may be effected before addition of the hydrolysable compounds of yttrium and manganese, iron, cobalt, nickel, copper or zinc but the coating process preferably involves mixing the zirconia slurry firstly with a 15 hydrolysable compound of titanium, zirconium, hafnium or aluminium and secondly with a hydrolysable compound of yttrium and a hydrolysable compound of manganese, iron, cobalt, nickel, copper or zinc.

The powdered product is eminently suitable for use in the manufacture of shaped ceramic bodies by firing.

The product in having the hydrous yttrium oxide stabilising agent and the hydrous oxide of manganese, 20 iron, cobalt, nickel, copper or zinc present as a coating provides a well distributed and intimate mixture of these oxides and on firing good incorporation of the oxides through the zirconia is achieved.

The use of hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc together with the hydrous yttrium oxide enables the production of zirconia-based ceramics with an improved resistance to aqueous degradation compared to those produced with a similar amount of yttrium oxide in the absence of at least 25 one of these oxides. The resistance to aqueous degradation can be demonstrated by measuring the strength of samples of ceramics after exposure to water under pressure at, for example, 180 °C. The invention provides a particularly convenient starting component for use in these ceramics.

The invention is illustrated by the following Examples.

30 **EXAMPLE 1**

Zirconia particles of approximately 0.1 μm (micron) diameter prepared by vapour phase oxidation of zirconium tetrachloride were dispersed in water at a concentration of 200 grams per litre. As a result of the reaction of residual Zr-Cl groups with the water the dispersion obtained had a pH value of 1.

35 An aqueous solution of acid zirconium sulphate (containing the equivalent of 100 grams per litre ZrO_2) was added to the dispersion in an amount sufficient to introduce hydrous zirconia in an amount of 1% by weight of ZrO_2 on solids. To the dispersion so obtained sufficient aqueous solution of yttrium chloride (containing the equivalent of 180 grams per litre Y_2O_3) to introduce 4.7% by weight Y_2O_3 based on solids was added followed by sufficient aqueous solution of copper (II) sulphate to introduce 0.07% by weight CuO 40 based on solids. The pH was then raised by the addition of aqueous sodium hydroxide over a period of 10 minutes to a value of 8.0 and the dispersion stirred for a further 30 mins at room temperature.

The coated zirconia was then separated by filtration, washed with deionised water and dried at 110 °C.

EXAMPLE 2

45 Zirconia particles similar to those used in Example 1 were coated with zirconia, yttria and iron oxides in a manner similar to that used in Example 1 except that, in place of the copper (II) sulphate, an amount of iron (II) sulphate sufficient to introduce 0.25% by weight FeO based on solids was used. After coating the zirconia was separated by filtration, washed with deionised water, and dried at 110 °C.

50 **Testing of Products**

Portions of coated zirconia produced as described in Examples 1 and 2 were formed into discs of approximately 30 mm diameter by single ended die-pressing at 30 MPa. Discs were also prepared for 55 comparison from zirconia bearing a coating of zirconia and yttria produced by a method similar to that used in Examples 1 and 2 but without the addition of either copper or iron salt. (Control).

The discs were fired at 1300 °C, their surfaces polished and the strength (Modulus of Rupture) of 10 discs was measured by a three-point biaxial flexure test.

Batches of 10 sintered discs were immersed in distilled water in an autoclave at 180 °C and a pressure of 10.0 bar, following the method of Nakajima et al, Advances in Ceramics, Vol. 12 pages 399-403 (1984) to determine their resistance to aqueous degradation.

Strength measurements were made on the exposed samples using a three-point biaxial flexure test, 5 values obtained being on single samples. Results are given below in Table 1.

TABLE 1

10	Exposure Time (hrs)	Fracture Strength (MPa)		
		Control	EXAMPLE 1	EXAMPLE 2
15	0	1444	1368	1558
	4	1170	1440	1523
	24	1229	1200	1346
	50	1165	1218	1426
	100	1285	1279	1473
	200	1057	1207	1408
	320	826	1131	1374
20	500	131	1167	1355
	1000	51	1119	1421

These results demonstrate the ability of ceramic bodies prepared from powders produced according to Example 1 or Example 2 to resist aqueous degradation. This resistance is an improvement by comparison 25 with the control sample which represents a ceramic considered to possess good resistance to aqueous degradation.

Claims

- 30 1. A composition suitable for use in the manufacture of a ceramic material comprising particulate zirconia characterised in that the particles are coated with a hydrous oxide of yttrium and a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.
2. A composition according to claim 1 characterised in that the majority of the particles have a diameter of not greater than 0.5 µm (micron).
3. A composition according to claim 1 or 2 characterised in that the amount of hydrous oxide of yttrium present on the particles is from about 10% to about 20% by weight hydrous oxide of yttrium expressed as Y₂O₃ based on weight of zirconia.
- 40 4. A composition according to claim 1 to 2 characterised in that the amount of hydrous oxide of yttrium present on the particles is from about 2% to about 10% by weight hydrous oxide of yttrium expressed as Y₂O₃ based on weight of zirconia.
- 45 5. A composition according to any one of the preceding claims characterised in that the amount of hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc present on the particles is from about 0.01 molar % to about 4.0 molar % expressed as Mn, Fe, Co, Ni, Cu or Zn based on zirconia.
- 50 6. A composition according to claim 5 characterised in that the amount of hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc is from about 0.05 molar % to about 1.0 molar %.
7. A composition according to any one of the preceding claims characterised in that a coating of hydrous titania, zirconia, hafnia or alumina is present on the particles of zirconia.
- 55 8. A composition according to claim 7 characterised in that the coating of hydrous titania, zirconia, hafnia or alumina forms an inner coating on the zirconia particles and the hydrous yttrium oxide and hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc form an outer coating.

9. A composition according to any one of the preceding claims characterised in that the hydrous yttrium oxide is present as a separate layer distinct from the layer of hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.
- 5 10. A composition according to any one of the preceding claims characterised in that the particulate zirconia is formed by the vapour phase oxidation and/or hydrolysis of a vapourised zirconium compound.
11. A composition according to claim 10 characterised in that the oxidation is carried out by oxidising 10 zirconium tetrachloride with oxygen which has been heated by means of an electric plasma.
12. A composition according to any one of the preceding claims characterised in that the composition contains less than 0.01% by weight alkali metal impurity expressed as M_2O .
- 15 13. A process for preparing a composition suitable for use in the manufacture of a ceramic material characterised in that particles of zirconia are dispersed in water, a water soluble hydrolysable compound of yttrium and a water soluble hydrolysable compound of manganese, iron, cobalt, nickel, copper or zinc is added and the pH of the dispersion is adjusted to coat the particles with a hydrous oxide of yttrium and a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.
- 20 14. A process according to claim 13 characterised in that the dispersion of zirconia particles formed is acidic.
15. A process according to claims 13 or 14 characterised in that the concentration of zirconia in the 25 dispersion is from 50 to 400 grams per litre.
16. A process, according to any one of claims 13 to 15 characterised in that the degree of dispersion is improved by milling.
- 30 17. A process according to any one of claims 13 to 16 characterised in that the water soluble compound of yttrium and the water soluble compound of manganese, iron, cobalt, nickel, copper or zinc are added to the dispersion before the pH is adjusted.
18. A process according to any one of claims 13 to 17 characterised in that the coating process is carried 35 out at a temperature of from 10°C to 70°C.
19. A process according to any one of claims 13 to 18 characterised in that the pH is adjusted to from 3 to 12.
- 40 20. A process according to any one of claims 13 to 19 characterised in that the pH is adjusted with ammonia.
21. A process according to any one of claims 13 to 20 in which an inner coating of a hydrous oxide of 45 titanium, zirconium, hafnium, or aluminium is formed on the particles of zirconia by adding a water soluble hydrolysable compound of titanium, zirconium, hafnium or aluminium to the dispersion and adjusting the pH of the dispersion.
22. A ceramic article formed from particulate zirconia the particles of which have been coated with a hydrous oxide of yttrium and a hydrous oxide of manganese, iron, cobalt, nickel, copper or zinc.

50 **Patentansprüche**

1. Zusammensetzung, geeignet zur Verwendung bei der Herstellung eines Keramikmaterials, umfassend teilchenförmiges Zirkoniumoxid, dadurch gekennzeichnet, 55 daß die Teilchen mit einem wasserhaltigen yttriumoxid und einem wasserhaltigen Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink beschichtet sind.

2. Zusammensetzung nach Anspruch 1,
dadurch gekennzeichnet,
daß der Großteil der Teilchen einen Durchmesser von nicht mehr als 0,5 μm (Mikrometer) aufweist.
- 5 3. Zusammensetzung nach Anspruch 1 oder 2,
dadurch gekennzeichnet,
daß die auf den Teilchen vorhandene Menge von wasserhaltigem Yttriumoxid von etwa 10 bis etwa 20 Gew.-% wasserhaltiges Yttriumoxid, ausgedrückt als Y_2O_3 , bezogen auf das Gewicht von Zirkonium-oxid, beträgt.
- 10 4. Zusammensetzung nach Anspruch 1 oder 2,
dadurch gekennzeichnet,
daß die auf den Teilchen vorhandene Menge von wasserhaltigem Yttriumoxid von etwa 2 % bis etwa 10 Gew.-% wasserhaltiges Yttriumoxid, ausgedrückt als Y_2O_3 , bezogen auf das Gewicht von Zirkonium-oxid, beträgt.
- 15 5. Zusammensetzung nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet,
daß die auf den Teilchen vorhandene Menge von wasserhaltigem Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink von etwa 0,01 Mol-% bis etwa 4,0 Mol-%, ausgedrückt als Mn, Fe, Co, Ni, Cu oder Zn, bezogen auf Zirkoniumoxid, beträgt.
- 20 6. Zusammensetzung nach Anspruch 5,
dadurch gekennzeichnet,
daß die Menge von wasserhaltigem Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink von etwa 0,05 Mol-% bis etwa 1,0 Mol-% beträgt.
- 25 7. Zusammensetzung nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet,
daß auf den Zirkoniumoxidteilchen eine Beschichtung von wasserhaltigem Titanoxid, Zirkoniumoxid, Hafniumoxid oder Aluminiumoxid vorhanden ist.
- 30 8. Zusammensetzung nach Anspruch 7,
dadurch gekennzeichnet,
daß die Beschichtung von wasserhaltigem Titanoxid, Zirkoniumoxid, Hafniumoxid oder Aluminiumoxid auf den Zirkoniumoxidteilchen eine innere Beschichtung bildet und daß das wasserhaltige Yttriumoxid und das wasserhaltige Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink eine äußere Beschichtung bildet.
- 35 40 9. Zusammensetzung nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet,
daß das wasserhaltige Yttriumoxid als eine separate, von der Schicht von wasserhaltigem Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink getrennte Schicht vorhanden ist.
- 45 10. Zusammensetzung nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet,
daß das teilchenförmige Zirkoniumoxid durch die Dampfphasenoxidation und/oder Hydrolyse einer verdampften Zirkoniumverbindung gebildet wird.
- 50 11. Zusammensetzung nach Anspruch 10,
dadurch gekennzeichnet,
daß die Oxidation durchgeführt wird durch Oxidieren von Zirkoniumtetrachlorid mit Sauerstoff, der mittels eines elektrischen Plasmas erwärmt wurde.
- 55 12. Zusammensetzung nach einem der vorhergehenden Ansprüche,
dadurch gekennzeichnet,
daß die Zusammensetzung weniger als 0,01 Gew.-% Alkalimetallverunreinigungen, ausgedrückt als M_2O enthält.

13. Verfahren zum Herstellen einer zur Verwendung bei der Herstellung eines Keramikmaterials geeigneten Zusammensetzung,
dadurch gekennzeichnet,
daß Zirkoniumoxidteilchen in Wasser dispergiert werden, eine wasserlösliche hydrolysierbare Yttriumverbindung und eine wasserlösliche hydrolysierbare Verbindung von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink zugegeben wird, und der pH-Wert der Dispersion eingestellt wird, um die Teilchen mit einem wasserhaltigen Yttriumoxid und einem wasserhaltigen Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink zu beschichten.

10 14. Verfahren nach Anspruch 13,
dadurch gekennzeichnet,
daß die aus Zirkoniumoxidteilchen gebildete Dispersion sauer ist.

15 15. Verfahren nach Anspruch 13 oder 14,
dadurch gekennzeichnet,
daß die Konzentration von Zirkoniumoxid in der Dispersion von 50 bis 400 Gramm pro Liter beträgt.

20 16. Verfahren nach einem der Ansprüche 13 bis 15,
dadurch gekennzeichnet,
daß der Dispergierungsgrad durch Mahlen verbessert wird.

25 17. Verfahren nach einem der Ansprüche 13 bis 16,
dadurch gekennzeichnet,
daß die wasserlösliche Yttriumverbindung und die wasserlösliche Verbindung von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink zu der Dispersion zugegeben werden, bevor der pH-Wert eingestellt wird.

30 18. Verfahren nach einem der Ansprüche 13 bis 17,
dadurch gekennzeichnet,
daß das Beschichtungsverfahren bei einer Temperatur von 10 °C bis 70 °C durchgeführt wird.

35 19. Verfahren nach einem der Ansprüche 13 bis 18,
dadurch gekennzeichnet,
daß der pH-Wert auf 3 bis 12 eingestellt wird.

20 20. Verfahren nach einem der Ansprüche 13 bis 19,
dadurch gekennzeichnet,
daß der pH-Wert mit Ammoniak eingestellt wird.

40 21. Verfahren nach einem der Ansprüche 13 bis 20, wobei eine innere Beschichtung eines wasserhaltigen Oxids von Titan, Zirkonium, Hafnium oder Aluminium auf den Zirkoniumoxidteilchen gebildet wird durch Zugeben einer wasserlöslichen hydrolysierbaren Verbindung von Titan, Zirkonium, Hafnium oder Aluminium zur Dispersion und Einstellen des pH-Werts der Dispersion.

45 22. Keramikgegenstand, gebildet aus teilchenförmigem Zirkoniumoxid, wobei dessen Teilchen mit einem wasserhaltigen Oxid von Yttrium und einem wasserhaltigen Oxid von Mangan, Eisen, Kobalt, Nickel, Kupfer oder Zink beschichtet wurden.

Revendications

50 1. Composition adaptée pour une utilisation dans la production d'une matière céramique comprenant de la zircone partiaire, caractérisée en ce que les particules sont revêtues d'un oxyde hydraté d'yttrium et d'un oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc.

55 2. Composition selon la revendication 1, caractérisée en ce que la majorité des particules a un diamètre inférieur ou égal à 0,5 µm (microns).

3. Composition selon la revendication 1 ou 2, caractérisée en ce que la quantité d'oxyde hydraté d'yttrium présent sur les particules est comprise entre environ 10% et environ 20% en masse d'oxyde hydraté d'yttrium, exprimée en Y_2O_3 , par rapport à la masse de la zircone.
- 5 4. Composition selon la revendication 1 ou 2, caractérisée en ce que la quantité d'oxyde hydraté d'yttrium présent sur les particules est comprise entre environ 2% et environ 10% en masse d'oxyde hydraté d'yttrium, exprimée en Y_2O_3 , par rapport à la masse de la zircone.
- 10 5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la quantité d'oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc présent sur les particules est comprise entre environ 0,01% en mole et environ 4,0% en mole, exprimée en Mn, Fe, Co, Ni, Cu ou Zn, par rapport à la zircone.
- 15 6. Composition selon la revendication 5, caractérisée en ce que la quantité d'oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc est comprise entre environ 0,05% en mole et environ 1,0% en mole.
- 20 7. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce qu'un revêtement de dioxyde de titane hydraté, zircone hydratée, oxyde d'hafnium hydraté ou oxyde d'aluminium hydraté est présent sur les particules de zircone.
- 25 8. Composition selon la revendication 7, caractérisée en ce que le revêtement de dioxyde de titane hydraté, zircone hydratée, oxyde d'hafnium hydraté ou oxyde d'aluminium hydraté forme un revêtement interne sur les particules de zircone et en ce que l'oxyde hydraté d'yttrium et l'oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc forment un revêtement externe.
- 30 9. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que l'oxyde hydraté d'yttrium est présent sous la forme d'une couche séparée distincte de la couche d'oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc.
- 35 10. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la zircone particulière est formée par oxydation et/ou hydrolyse en phase vapeur d'un composé de zirconium vaporisé.
- 40 11. Composition selon la revendication 10, caractérisée en ce qu'on met en oeuvre l'oxydation en oxydant du tétrachlorure de zirconium avec de l'oxygène qui a été chauffé à l'aide d'un plasma électrique.
12. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que la composition contient moins de 0,01% en masse d'impureté de métal alcalin exprimée en M_2O .
- 45 13. Procédé de préparation d'une composition adaptée pour une utilisation dans la production d'une matière céramique, caractérisé en ce qu'on disperse dans l'eau les particules de zircone, en ce qu'on ajoute un composé hydrolysable soluble dans l'eau d'yttrium et un composé hydrolysable soluble dans l'eau de manganèse, fer, cobalt, nickel, cuivre ou zinc et en ce qu'on ajuste le pH de la dispersion pour revêtir les particules d'un oxyde hydraté d'yttrium et d'un oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc.
14. Procédé selon la revendication 13, caractérisé en ce que la dispersion des particules de zircone formées est acide.
- 50 15. Procédé selon les revendications 13 ou 14, caractérisé en ce que la concentration de zircone dans la dispersion est comprise entre 50 et 400 g/l.
16. Procédé selon l'une quelconque des revendications 13 à 15, caractérisé en ce que le degré de dispersion est amélioré par broyage.
- 55 17. Procédé selon l'une quelconque des revendications 13 à 16, caractérisé en ce qu'on ajoute à la dispersion le composé soluble dans l'eau d'yttrium et le composé soluble dans l'eau de manganèse,

fer, cobalt, nickel, cuivre ou zinc avant d'avoir ajusté le pH.

18. Procédé selon l'une quelconque des revendications 13 à 17, caractérisé en ce qu'on met en œuvre le procédé de revêtement à une température comprise entre 10 °C et 70 °C.

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19. Procédé selon l'une quelconque des revendications 13 à 18, caractérisé en ce qu'on ajuste le pH entre 3 et 12.

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20. Procédé selon l'une quelconque des revendications 13 à 19, caractérisé en ce qu'on ajuste le pH avec de l'ammoniac.

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21. Procédé selon l'une quelconque des revendications 13 à 20, dans lequel on forme un revêtement interne d'un oxyde hydraté de titane, zirconium, hafnium ou aluminium sur les particules de zircone en ajoutant un composé hydrolysable soluble dans l'eau de titane, zirconium, hafnium ou aluminium à la dispersion et en ajustant le pH de la dispersion.

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22. Article en céramique formé à partir de la zircone particulière dont les particules ont été revêtues d'un oxyde hydraté d'yttrium et d'un oxyde hydraté de manganèse, fer, cobalt, nickel, cuivre ou zinc.

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